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A INVESTIGATION OF
NEGATIVE ION PRODUCTION

by

John Albert Schira Jr

Leo Warren Stockham

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NEGATIVE ION PRODUCTION

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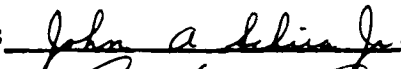
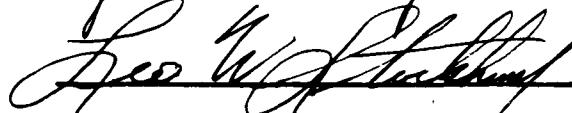
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AN INVESTIGATION OF
NEGATIVE ION PRODUCTION

by

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of Science respectively.

ABSTRACT

The ionization of high electron affinity gases on low work function surfaces has recently been the subject of intensive investigation due to its application to electrostatic thrusting devices. The object of this study was to research the problems involved in negative ion production and attempt to select a specific combination of low work function surface and high electron affinity gas for efficient negative ion production. Phosphorus gas on a thoriated tungsten filament was chosen. The equations governing the physics of the problem are included with an explanation of their application. To accomplish the experimental part of the study, a vacuum tube was designed and constructed. The tube contained a sealed vial of phosphorus and a thoriated tungsten filament. It was intended to break the phosphorus vial after the filament was activated and vary wire temperature and bath temperature to study their effect upon ion production. The filament could not be activated however, and the experimental part of this study could not be completed. The main body of this report therefore consists of an account of the theoretical foundation which governs the production of negative ions

and the evolution of a vacuum tube design to investigate this phenomena. In addition, a lengthy discussion of the various work functions is included with special reference to their involvement in the Saha-Langmuir equations and the electron emission equation. The report also contains information on the methods of placing white phosphorus in sealed, evacuated ampules. Finally, suggestions are made to facilitate further investigation into the experimental phase of this report.

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SYMBOLS

<u>Symbol</u>	<u>Meaning</u>
A	atomic electron affinity
I	current
j	current density
k	Boltzmann's constant
m	mass of a particle
mfp	mean free path
N	number of atoms per molecule
n	molecular concentration
r	quantum mechanical reflection and radius
torr	millimeters of mercury
T_s	surface temperature
T_v	vapor temperature
w	statistical weight
ϕ	true work function
ϕ_a	active work function
ϕ_e	effective work function
ϕ_i	atomic ionization potential

CHAPTER 1

INTRODUCTION

1.1 Motivation

The primary motivation for our experimentation with negative ion production stems from the need for neutralization of the expellant of electrostatic thrusting devices. Electron injection into the exhaust stream is the method currently used with positive ion engines. Analyses of power efficiency and neutralizing effectiveness of electron injection systems indicate that there may be a method available which is superior to that utilizing electrons as the neutralizing agent.¹ If a simple means of producing a stable negative ion could be devised, the neutralization problem might be solved while simultaneously producing useful thrust through acceleration of the negative ions. The results of research on positive ion thrusting devices can be applied to those utilizing negative ions. Obtaining the negative ion is yet another problem.

1.2 Background

A great deal of research has recently been devoted

to the investigation of negative ion production by surface ionization.² When producing a negative ion by this means, it is necessary to combine a high electron affinity gaseous substance with a stable low work function surface. The halogens are very popular as the high electron affinity gaseous substance, iodine being the foremost choice. Thoriated tungsten³ and various oxides⁴ are among the more common low work function surfaces.

When the gas and low work function surface are combined to form negative ions, problems arise which cannot be accurately predicted. An activated thoriated tungsten surface is highly susceptible to "poisoning" by electronegative gases and oxide coatings seem to be susceptible to attack by various gaseous products. Some types of surfaces suffer material failure at temperatures below the minimum temperature required to fully dissociate the gas molecules and are therefore unsuitable.² To our knowledge no combination of low work function surface and high electron affinity gas which gives sufficiently high ionization efficiency to be utilized as a propulsion system has yet been found. For this reason we have endeavored to investigate the feasibility of producing negative ions by bringing phosphorous gas into contact with an activated thoriated tungsten surface.

1.3 Preparation

Since a suitable apparatus was not available, it was

necessary to design and construct a vacuum tube which would satisfy the needs of the experiment. The tube which evolved was patterned after the apparatus used by Langmuir and Taylor in their investigation of cesium on tungsten.⁵ Modifications were incorporated in accordance with the fundamental differences between the two experiments. A complete description of the apparatus is given in Chapter 3.

CHAPTER 2

THEORETICAL FOUNDATION

2.1 General

The main objective of this investigation was to ascertain whether the combination of phosphorous and thoriated tungsten could efficiently produce negative ions. To accomplish this it was necessary to relate electron currents and negative ion currents to the temperature of the low work function surface and the temperature and pressure of the gas. The vacuum tube apparatus provides a suitable environment in which to investigate these relationships. The equations which describe the experiment are presented in what follows. In those cases where geometry of the apparatus is a factor, the equations are specialized to fit our apparatus.

2.2 Surface Ionization

The process of converting gas molecules to negative atomic ions has two distinct steps. The first is the dissociation of the molecule into atoms and the second is ionization of the atoms. The dissociation process is essentially temperature dependent. For this reason it can

be assumed that above some minimum surface temperature, the dissociation at the surface will be complete.

Assuming sufficient surface temperature for complete dissociation, the atoms on the surface can leave as negative ions, positive ions, or atoms. The ratios of the ion and atom currents can be expressed by the following modified forms of the Saha-Langmuir equations

$$\frac{I_+}{I_n} = \frac{w_+(1-r_+)}{w_n(1-r_n)} \exp (\phi - \phi_i) / kT_s \quad (2.1)$$

$$\frac{I_-}{I_n} = \frac{w_-(1-r_-)}{w_n(1-r_n)} \exp (A - \phi) / kT_s \quad (2.2)$$

where +, -, and n subscripts denote positive ion, negative ion, and atom respectively, I is the current from the surface, w the statistical weight, A the atomic electron affinity, ϕ_i the atomic ionization potential, ϕ the true work function of the surface, k Boltzmann's constant, and T_s the surface or filament temperature.^{5,6} The quantum mechanical reflection r, is usually considered zero. Filament temperature was determined from the data compiled by Jones and Langmuir.⁷

A brief look at the quantities involved in these equations indicates what material properties are desirable for efficient negative ion production. The ratios of statistical weights are typically $\frac{1}{2}$ or 1 and as mentioned, quantum mechanical reflection is usually neglected. An average surface temperature might be 1200° K, making kT_s approxi-

mately 0.1 electron volts. Using these values, equation 2.1 shows that to suppress positive ion production we need an atom with a high ionization potential and a surface with a low work function. Similarly, equation 2.2 shows that for a high ratio of negative ions to neutrals leaving the surface, it is necessary to have an atom with a high electron affinity and a surface with a low work function. The tables in Appendix C give values for true work function, electron affinity, and ionization potential for some common surfaces and atoms.

The choice of phosphorus, $A=4.03$ ev, $\phi_1=10.55$ ev, and thoriated tungsten, $\phi=3.0$ ev gives the following ratios

$$\frac{I_+}{I_n} = \frac{1}{2} e^{-75.5} , \quad \frac{I_-}{I_n} = \frac{1}{2} e^{+10.3} .$$

Therefore, from this standpoint, phosphorus on a thoriated tungsten surface should be an efficient negative ion source.

2.3 The Effective Work Function

The term "work function" has been used to describe many different quantities. As a result, there appears to be some confusion as to which of these quantities should be used in the Saha-Langmuir equations presented in the previous section. Much of this confusion would be eliminated if all low work function surfaces were perfectly homogeneous in nature. However, since most surfaces have microscopic variations in their properties, some averaging process must be used to obtain a macroscopic description of a

given surface.

One such averaging process for weighting the microscopic deviations of the true work function of a surface is suggested by the Saha-Langmuir equations. If the total positive ion current, the total atom current, and all other quantities except ϕ were obtained for a large surface area, an "average" value of the true work function over the surface could be obtained by applying equation 2.1. This work function will be called the active work function, ϕ_a . This work function is perfectly satisfactory for use in the Saha-Langmuir equations but is limited in its application to other phenomena such as electron emission.

The equation describing electron emission

$$j = 120(T_s)^2 \exp(-\phi/kT_s) \quad (2.3)$$

where j is the emitted electron current density in amps per square centimeter and T_s is the emitter surface temperature, is another relationship which can be used to obtain a weighted value of the microscopic distribution of the true work function. This is accomplished by measuring the total current from a large area of the surface and dividing by that area to obtain a current density. This value of j is then attributed to some "average" work function distributed over the entire surface. The work function obtained in this manner is called the effective work function ϕ_e , and is not necessarily the same as ϕ_a . However, since ϕ_a can be found only by measuring a phenomena we wish to predict and

since ϕ_e has been shown to be somewhat in agreement with ϕ_a , ϕ_e can be used in the Saha-Langmuir equations for a rough approximation of expected ionization efficiencies.² For further discussion of the various work functions, see Appendix A.

2.4 Space Charge Limited Current

The current density which can exist between two electrodes is limited by a phenomena known as space charge. The space charge limited current for singly ionized atoms or electrons flowing between concentric cylindrical electrodes has been shown to be

$$i = \frac{2\sqrt{2}}{9} \frac{e}{m} \frac{V_c}{r}^{3/2} \quad (2.4)$$

where m is the mass of the particle, V_c the collector voltage, r the collector radius, and i the current per unit length.⁸ The ratio of collector diameter to filament diameter is assumed greater than twenty.

In designing a vacuum tube such as the one used in this experiment, consideration must be given to the available voltage sources, the capabilities of current measuring devices, and the physical bulk of the apparatus. Trade off among these parameters as well as considerations discussed in section 2.6 established the radius of the tube at one centimeter.

2.5 Maximum Ion Current

If conditions are such that all arriving atoms leave the filament as negative ions, and no space charge limitation is encountered, the maximum current between the filament and the collector can be evaluated in terms of the properties of the gas. From kinetic theory the number of gas molecules arriving per unit filament area per second is

$$I_n = p / \sqrt{2\pi m k T_v} \quad (2.5)$$

where p is the vapor pressure, m the mass of the molecule, and T_v the temperature of the gas. Assuming that there are N atoms in each arriving molecule and that all these atoms leave as ions, the resulting current density is expressed by

$$(I_-)_{\max} = NeI_n \quad (2.6)$$

where e is the electron charge.

A table of the vapor pressure of phosphorus appears in Appendix C. For temperatures under 800° Kelvin the vapor consists mainly of P_4 molecules. Therefore at 403° K, which was a reasonable temperature for the available ovens, a maximum current of .0201 amps/cm² could be expected. The available ammeters covered the range from one microampere to one ampere. Therefore it was decided to select a filament area and collector combination which would give a current of approximately one milliampere. The two mil filament with current collected from the center three centimeters gave a

predicted maximum current of .962 milliamperes.

2.6 Control of Arrival Rate

To effectively maintain an ion current, it is necessary to establish a constant arrival rate of atoms to the surface and hence a constant molecular current density throughout the tube. From equation 2.5 it is apparent that a constant I_n requires a constant ratio of $p/\sqrt{T_v}$. In addition, it can be shown that if the mean free path of the gas molecules is large compared to the tube radius, particle with wall collisions will dominate and pressure gradients cannot exist in the tube. Further, most elements have a unique temperature versus vapor pressure relationship so that for a given temperature of the solid (or liquid) form of the element, the vapor pressure is uniquely determined. These considerations suggest a means for controlling the arrival rate.

If a sufficient amount of the element to be ionized is introduced into the tube, some of it will remain in the solid (or liquid) state. Then, if the temperature of all of the solid (or liquid) can be uniquely controlled, the pressure throughout the tube is determined, provided the mean free path is large.

To investigate the magnitude of the mean free path, the expression

$$mfp = \frac{1}{\pi n D^2} \quad (2.7)$$

where D is the molecular diameter and n the molecular concentration was used.⁹ The values obtained were then used to place maximum limits on operating pressures for given tube dimensions. By trade off between tube size and pressure, tube dimensions were selected and hence an upper limit on operating pressure established.

Control of the temperature of the solid in the tube was affected by controlling the temperature of the tube walls. Since the collector electrodes were painted on the tube wall, all places where the solid could accumulate were in intimate contact with the tube walls. Hence control of wall temperature by a bath would effectively determine the solid temperature.

CHAPTER 3

DESCRIPTION OF FIRST APPARATUS

The vacuum tube was essentially the same as that used by Taylor and Langmuir in their experiments with cesium on a tungsten wire.⁵ Some simplifications were made due to the different nature of our experiment. For instance, since phosphorus is a non-conductor, it was unnecessary to put annular folds in the tube for insulation between the three collector rings. We also found it expedient to eliminate the second lead on each collector ring. This proved to be a mistake since it was impossible to check the continuity of the lead-in connection after the tube was assembled. The first tube looked like that in Figure 1.

The vacuum tube was constructed in several steps. Initially a straight, open-ended glass barrel was constructed with three tungsten pins sealed in glass presses. Wires were led from the pins to small strips of platinum fused to the tube wall. The collector and guard rings were then painted on the tube wall with platinum paint. Care was taken to insure good coverage of the platinum strips. This assembly was then baked (not under vacuum) at 350° C to bake the platinum paint on the wall. The

connections for the vacuum pump and the capsule arm (see Figure 1) were placed on the main barrel after the filament was inserted.

The filament consisted of 30 centimeters of 2 mil wire. On each end a spring was formed by winding ten centimeters of the wire around a one millimeter mandril. This left a center section of straight wire 10 centimeters long. The resultant filament was approximately 14 centimeters long. When mounted, it was stretched $\frac{1}{2}$ centimeter to take up any expansion when heated. The two ends of the filament were welded to tungsten lead pins which were then sealed in end bells fused to the main tube barrel. After side arm attachments were made, the tube was evacuated to 10^{-6} torr at a temperature of 450° C.

CHAPTER 4

EXPERIMENT 1

After the tube preparation described in Chapter 3 and prior to sealing off from the vacuum pump, the filament was aged at 2800° K for 30 seconds. This caused the springs to become ineffective, allowing the filament to sag. The spring used to keep the filament taut in apparatus 2 was more carefully designed to prevent this from occurring again. The tube was then sealed off and the test circuit set up. Wire activation was attempted by heating the wire to 2100° K for three minutes. Measured electron emission indicated that the activation procedures had been unsuccessful. After several more unsuccessful attempts to activate, it was decided that the vacuum was not sufficient to prevent electro-negative gases from attacking the filament surface. This was later validated since a small leak was found in the nickel ampule container. Shortly hereafter the sag in the filament caused it to come into contact with the tube wall and the resulting short circuit destroyed apparatus 1.

CHAPTER 5

EXPERIMENT 2

5.1 Test Apparatus 2

The vacuum tube used in experiment two differed from tube number one in the following ways. Two leads were attached to each collector ring so that continuity checks were possible. The filament was suspended with a spring made according to the procedure recommended by Langmuir and Blodgett.¹⁰ Finally, a molybdenum getter assembly was included to help insure a vacuum sufficient to activate the filament. It was felt that these modifications would solve some of the problems encountered in experiment number one. See Figure 2.

5.2 Experiment Number 2

Upon completion of apparatus number two, it was evacuated, baked and the filament aged as in experiment one. The activation procedure was carried out but failed again. The tube was then placed on a leak detector and a small leak in the nickel tubing was discovered. The leak was small enough to be unnoticeable on the vacuum system, but large enough to be considered the probable cause of the

activation failures.

Because of time limitations, an attempt was made to seal the leak with red glyptol. The apparatus was then baked at 150° C and evacuated to 6×10^{-7} torr. While still on the vacuum system, the filament and getter were thoroughly outgassed by repeatedly passing the expected operating currents through them until no increase in pressure was noticeable on the ion gauge. The tube was then sealed off slowly, allowing the pump to remove the gas evolved during seal off.

Activation attempts were again unsuccessful. The getter was then fired several times putting a coat of molybdenum on the getter walls each time. Activation was tried again but was still unsuccessful. The getter was fired again until it vaporized completely, but still activation was impossible.

In a final attempt to activate the wire, the phosphorus ampule was broken and activation procedures carried out using phosphorus as a getter. The attempt was again unsuccessful.

By this time, it was apparent that either there was another leak in the tube or the glyptol had not sealed the first leak. In any event, activation was not going to occur. Therefore, it was decided to determine the work function which existed and to see what effect, if any, increased phosphorus vapor pressure would have upon it.

In the process of collecting data at elevated temp-

eratures, it became necessary to pass increasingly large currents through the filament. With a current of 1.3 amperes passing through them, the nickel leads to the spring vaporized, the filament fell against the collector and the resulting short circuit destroyed apparatus number two. The data collected prior to destruction of the apparatus is discussed in the following chapter.

CHAPTER 6

DATA

In this table, I_f and V_f will be filament current and voltage respectively, I_e will be emission current, and V_c will be the collector or anode voltage.

After firing the getter, the following data was taken.

$T_s(^{\circ}\text{K})$	$I_f(\text{amps})$	$V_f(\text{volts})$	$I_e(\text{milliamps})$	$V_c(\text{volts})$
2090	.400	17	.1	219
2010	.370	15	.03	219
1920	.340	12	.011	219
1820	.305	10	.0024	219
1640	.250	8	-	219

The wire had obviously not activated, so the following run was made after firing the getter again. ($V_c=219$ volts)

$T_s(^{\circ}\text{K})$	$I_f(\text{amps})$	$V_f(\text{volts})$	$I_e(\text{milliamps})$
2100	.405	16	.12
2030	.380	16	.045
1950	.350	13	.015
1850	.315	11	.003
1740	.280	9	-

Activation had still not occurred. At this point, the effectiveness of deflecting the electron current by a mag-

netic field was tested. 25 amperes of current through 30 turns of wire successfully deflected the electron emission current from the center collector to the outer two guard rings.

The capsule was now broken in an attempt to use the getter properties of phosphorus. Some red phosphorus was permitted to fall onto the wire and vaporize. This turned the red phosphorus to white phosphorus and hopefully the white phosphorus gettered the tube atmosphere somewhat.

The following data was taken with the red phosphorus capsule broken. The tube was at room temperature.

$T(^{\circ}K)$	I_f (amps)	V_f (volts)	I_e (milliamps)
1920	.9	34	.022
1990	.95	38	.084
2030	1.0	41	.200
2050	1.2	49.5	.62
2100	1.3	56	3.2

The following data was taken with the tube at $57^{\circ} C$.

I_f (amps)	V_f (volts)	I_e (milliamps)
.72	24.3	.00027
.86	31	.0059
.88	37	.049
.98	44.5	.571
1.2	57.0	3.4
1.3	(at this current the filament broke)	

CHAPTER 7

CONCLUSIONS

7.1 Data

Since activation of the thoriated tungsten filament was not accomplished, all data obtained was considered worthless as far as application to the behavior of phosphorus on an activated filament was concerned.

7.2 Tube Design

The most significant outcome of the work done prior to attempted filament activation was the design and construction of the apparatus. Since a leak can be encountered in any glass-metal construction, it can not be considered a fault of this particular design. The filament suspension system of apparatus 2 was effective from room temperature to 2800° K. The innovation of painting the electrodes on the tube wall also appeared to work quite well since only a negligible resistance, (about two ohms), could be measured between the two leads on each of the collector rings. The resistances from collector ring to collector ring were also measured after the getter had been fired and after the phosphorus ampule had been broken. At no time were any of

the electrodes shorted together. This not only justified the elimination of the annular folds used by Langmuir, but also established the fact that the getter would not deposit molybdenum vapor in the main tube on the electrodes.

7.3 Filament Activation

During the initial planning of the experiment, filament activation was considered a simple step towards a more complicated objective. Such was not the case since activation of a thoriated tungsten filament is a somewhat sophisticated process. Should further work be done on this experiment, it would be advisable to construct the main tube barrel without adding the sidearm for the capsule or getter tube. Activation procedures could then be run while still on the vacuum pump. This would allow the experimenter to gain familiarity with the activation process. After this is done the pumps could be turned off and the remainder of the tube assembled. Naturally, activation procedures would be rerun after tube assembly, pump down, and bake out.

7.4 A Problem in Negative Ion Engines

From the studies made during the course of this investigation, it has become obvious that there is a basic problem involved in producing negative ions which might be extremely difficult to overcome. Most gases of high electron affinity occur in molecular form. Before ionization

can occur, the molecule must be dissociated. This invariably demands a high temperature for the low work function surface. This causes high electron emission which cannot be tolerated in the optics of the ion engine. In addition, the power consumed by the electron emission is too high to be tolerated. This suggests finding a high electron affinity gas which occurs in atomic form at moderately low temperatures.

APPENDIX A

THE WORK FUNCTIONS

A.1 The True Work Function

The true work function of a point on a surface is defined as the energy difference between an electron at the fermi level of that point and an electron at rest at infinity, where no potential field exists outside the surface. This is the work which must be done to remove an electron from the surface. The magnitude of the true work function may vary from point to point due to surface impurities, different crystal orientation, and temperature variations. A complete description of the true work function for a surface would then require a detailed account of these surface variations. This is an extremely difficult, if not impossible expression to obtain. However, if this description were available, equations 2.1, 2.2. and 2.3 would be fulfilled by the parameters at any point on the surface within the limitations previously stated for these equations.

A.2 The Effective and Acting Work Functions

An alternative to the above scheme would be to mea-

sure a gross effect for a large surface and attribute it to some average work function. As discussed in section 2.3, the Saha-Langmuir equations or the electron emission equation can be used to accomplish this. The fallacy of assuming that ϕ_a the active work function obtained by the Saha-Langmuir equations, and ϕ_e its counterpart obtained by the electron emission equation are equal was also mentioned in section 2.3. We will now look into this further and attempt to gain some means of comparing ϕ_a and ϕ_e .

Let us assume a surface comprised of two sections of area A_1 and A_2 with constant true work functions ϕ_1 and ϕ_2 respectively. Reflectivity will be considered the same throughout and T_s will be considered constant over the surface. This derivation will then account for those variations in the ϕ due to all factors other than reflectivity and temperature variations.

Considering the electron emission equation first, we can compute an effective work function ϕ_e by measuring the total emission current from both A_1 and A_2 . This can then be equated to the actual contributions by A_1 and A_2 , finally defining ϕ_e in terms of ϕ_1 , ϕ_2 , A_1 , and A_2 . In equation form

$$\frac{1}{120(T_s)^2} = e^{-(\phi_e/kT_s)} = \frac{A_1}{A_1+A_2} e^{-(\phi_1/kT_s)} + \frac{A_2}{A_1+A_2} e^{-(\phi_2/kT_s)}$$

which resolves to

$$\phi_e = kT_s \ln \left[\frac{A_1 e^{-\phi_1/kT_s} + A_2 e^{-\phi_2/kT_s}}{A_1 + A_2} \right]^{-1} \quad (\text{A.1})$$

Now, to arrive at a similar expression for ϕ_a the acting work function, we measure the ratio of total positive ion current to total atom current for the entire surface and attribute it to ϕ_a . This can then be equated to the sum of the two contributions by A_1 and A_2 .

$$\begin{aligned} \frac{I_+ w_n (1 - r_n)}{I_n w_+ (1 - r_+)} &= \exp(\phi_a \phi_1) / kT_s \\ &= \frac{A_1 \exp(\phi_1 - \phi_1) / kT_s + A_2 \exp(\phi_2 - \phi_1) / kT_s}{A_1 + A_2} \end{aligned}$$

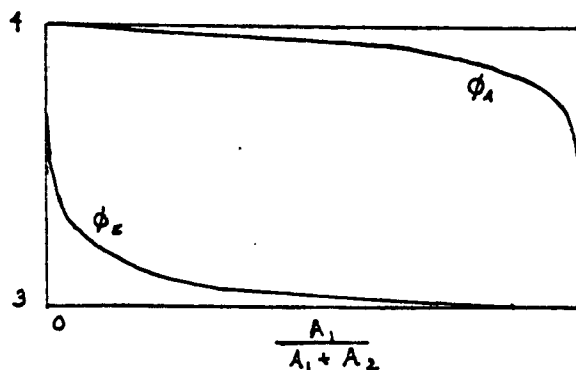
which reduces to

$$\phi_a = kT_s \ln \left[\frac{A_1 e^{\phi_1/kT_s} + A_2 e^{\phi_2/kT_s}}{A_1 + A_2} \right] \quad (\text{A.2})$$

The difference between equations A.1 and A.2 is obvious, but to see how this affects the surface it might be good to place some numbers in a simple example. Let us assume that we originally have a pure surface of true work function 4ev throughout and that for some reason, either intentionally or unintentionally, that surface begins to be either covered with another material or altered in some way so that the true work function of the affected area is reduced to 3ev. The affected area will be considered A_1 , the unaffected area A_2 . For these circumstances, the following is a table of ϕ_a and ϕ_e for various proportions of affected

area to total area. kT_s was assumed to be 0.1 ev.

$\frac{A_1}{A_1 + A_2}$	0	1/2000	1/148	1/100	1/40	1/10	1/2	9/10
ϕ_e	4.0	3.76	3.5	3.46	3.37	3.23	3.07	3.01
ϕ_a	4.0	4.0	4.0	4.0	3.998	3.99	3.93	3.77



We can see as soon as A_1 increases the slightest, ϕ_e is reduced and electron emission is enhanced, whereas the ratio of negative ions to neutral atoms still depends largely upon the original work function. Applying this to a low work function surface which has been constructed by surface coverage of a higher work function material, we see that electron emission is immediately enhanced whereas the efficient production of negative ions may still be in doubt. Here-in lies the danger of predicting ionization capability of a low work function surface from electron emission data.

It should also be noted that even for surfaces of a pure work function, this work function varies with temperature. This complicates the work function problem even further.

A.3 The Richardson Work Function

A fourth "work function" often encountered is the Richardson work function defined by

$$j = A_R T_s^2 e^{-\phi_R/kT_s} \quad (\text{A.3})$$

where j is the emitted electron current density, A_R is the Richardson constant which depends upon the material, T_s is the surface temperature, k is Boltzmann's constant, and ϕ_R is the Richardson work function for the material. A_R and ϕ_R are obtained by plotting $\ln (j/T_s^2)$ versus $1/T_s$ from experimental data. $-\phi_R/k$ is the slope and the $1/T_s = 0$ intercept is $\ln A_R$. The Richardson work function is not really a work function or even an average work function for the surface. It is merely a measure of the slope on a plotted curve of electron emission. Only when A_R is set equal to 120 does the Richardson work function vary with temperature and approach the meaning of a true work function. Strictly speaking this would no longer be called the Richardson work function.

APPENDIX B

PREPARATION OF WHITE PHOSPHORUS CAPSULES

One of the first problems encountered in the early stages of this experiment was that of obtaining small ampules of phosphorus at a moderate cost. White phosphorus was the first choice of element but was not available commercially in a suitable package. Red phosphorus was available but there was a considerable time lag between placing the order and delivery of the ampules. Therefore it was decided to attempt to make white phosphorus ampules, but to order the red phosphorus as a reserve. Vacuum distillation equipment was not available so another means of preparation was necessary. The method which evolved through several attempts and which was finally successful is described in the following paragraphs.

First and of primary importance is the matter of safety. White phosphorus ignites spontaneously and burns quite fiercely in air. Therefore one must take adequate precautions to insure protection against such possibilities as ampules of melted phosphorus exploding and showering the immediate area with burning liquid. The problem was solved by working in an open area and using asbestos aprons, arm

guards, and full face masks. On two occasions during early attempts, ampules exploded and burned. The safety precautions were adequate in both instances.

The method of filling the capsule is illustrated in Figure B.1. It utilizes the inertness of phosphorus under water and its low melting point (44° C). The procedure is to form, evacuate, bake and seal off an empty ampule assembly. Then to break off the tip in the melted phosphorus, let the pressure differential fill the capsule, and finally seal it off before removing the tip from the phosphorus. If carefully executed, this is a safe and effective method of producing white phosphorus capsules.

When the time came to assemble the vacuum tube, both red and white phosphorus ampules were available. The red phosphorus was used for two reasons. The first was that the empty ampule assemblies for white phosphorus had not been baked under high vacuum. Secondly, it had not been possible to adequately determine what impurities were present in the white phosphorus used to fill the ampules. Either of these factors could have destroyed the high vacuum of the tube. Therefore, since the commercial supplies had indicated that these factors would be eliminated from the red phosphorus ampules, red phosphorus was used. However, when pure white phosphorus and sufficient time to prepare the ampule assemblies are available, it is felt that the higher vapor pressures of white phosphorus warrant its use.

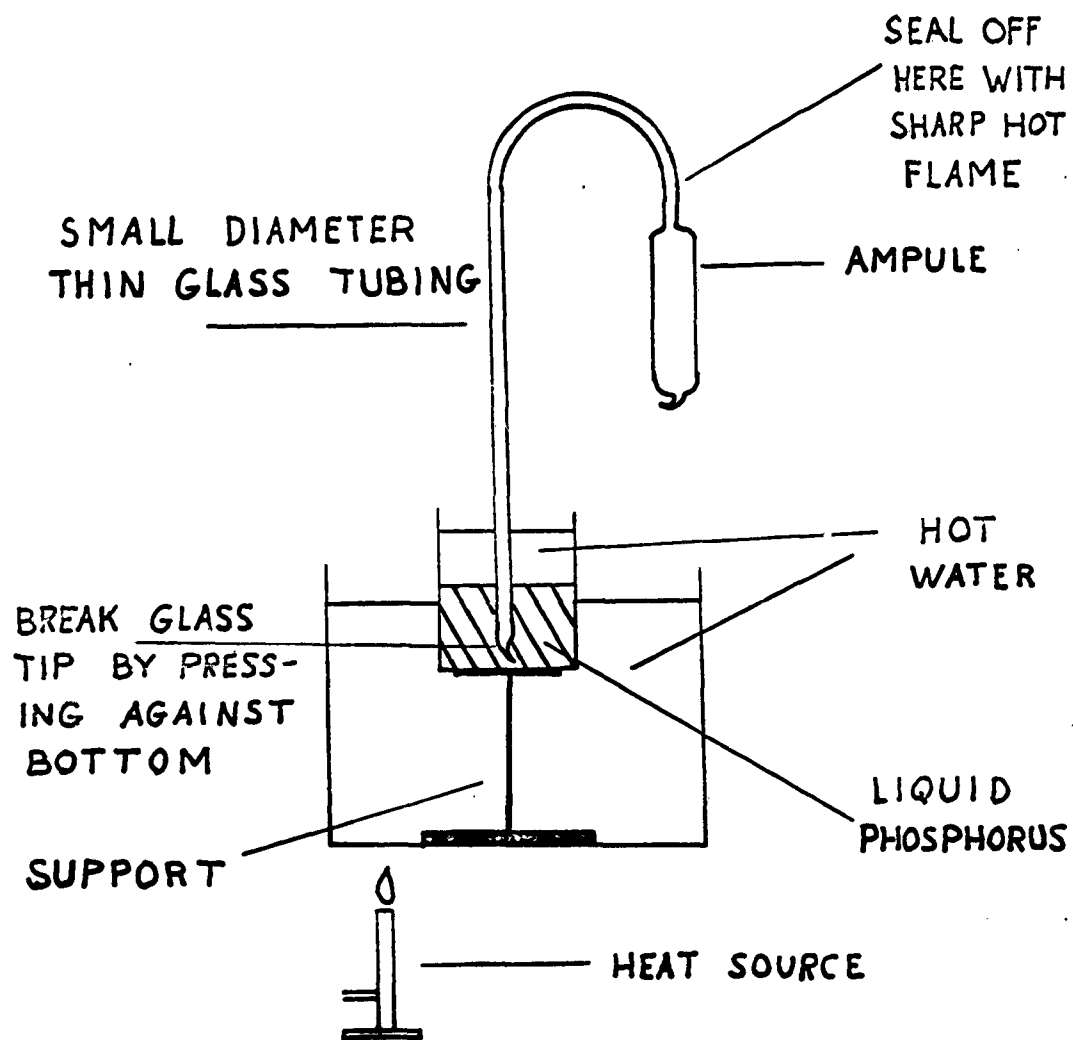


FIGURE B.I. PREPARATION
OF WHITE PHOSPHORUS
AMPULES

APPENDIX C

GAS	A	ϕ_i
F	3.62	17.418
P	4.03	10.55
S	2.07	10.357
H	0.754	13.595
C	1.13	11.264
I	3.23	10.44
Te	2.38	9.01
Se	1.73	9.75

(4)

SURFACE	ϕ
Ba	2.11
Ca	2.24
Cs	1.81
La	3.3
Pr	2.7
U	3.27
W	4.53
THOR. W	3.0

PHOSPHORUS VAPOR PRESSURE	
TEMP. °K	TORR
320	10^{-8}
335	10^{-7}
355	10^{-6}
380	10^{-5}
403	10^{-4}
430	10^{-3}
460	10^{-2}
495	10^{-1}
535	1
580	10

(11)

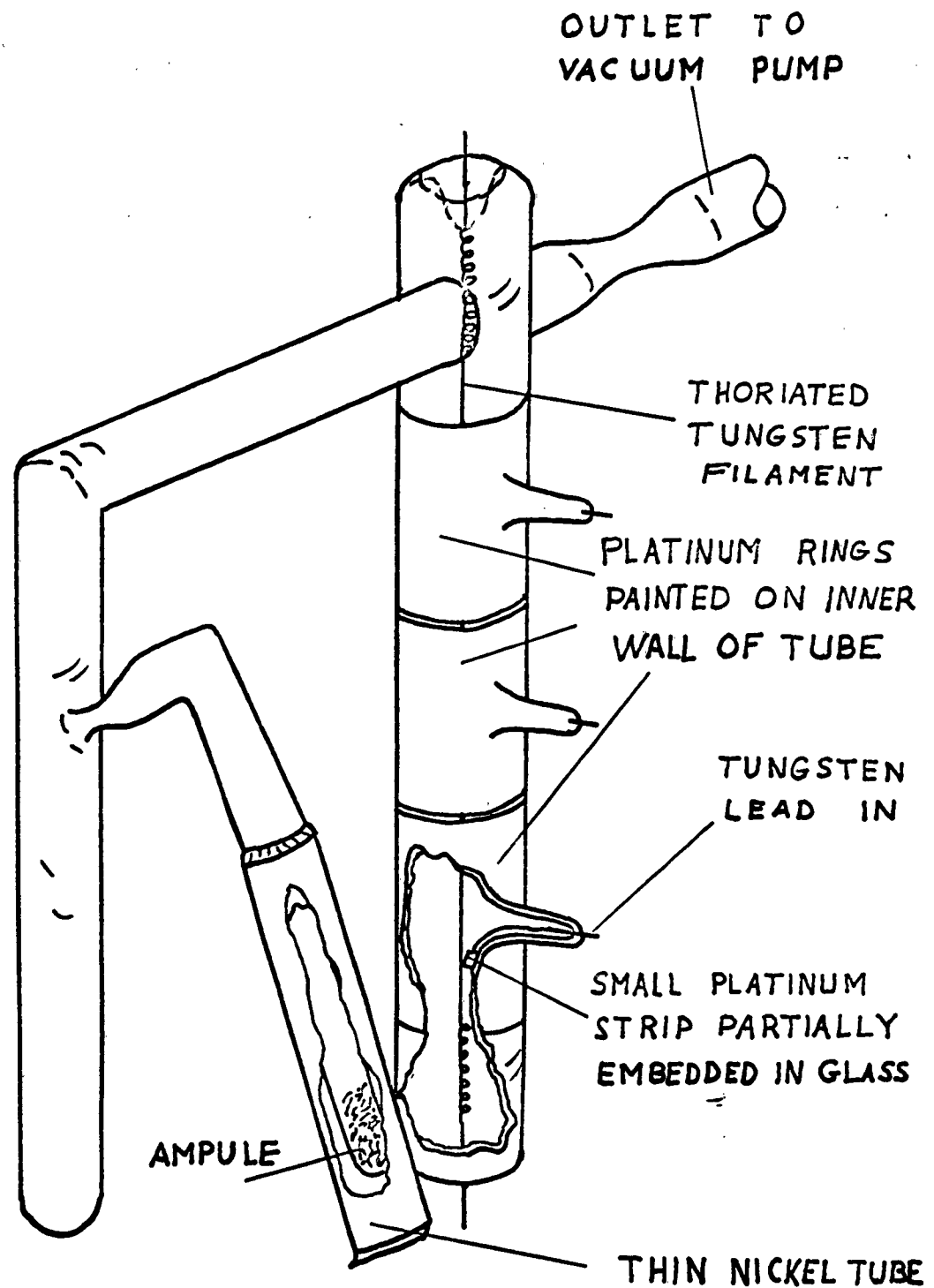


FIGURE 1 FIRST TUBE

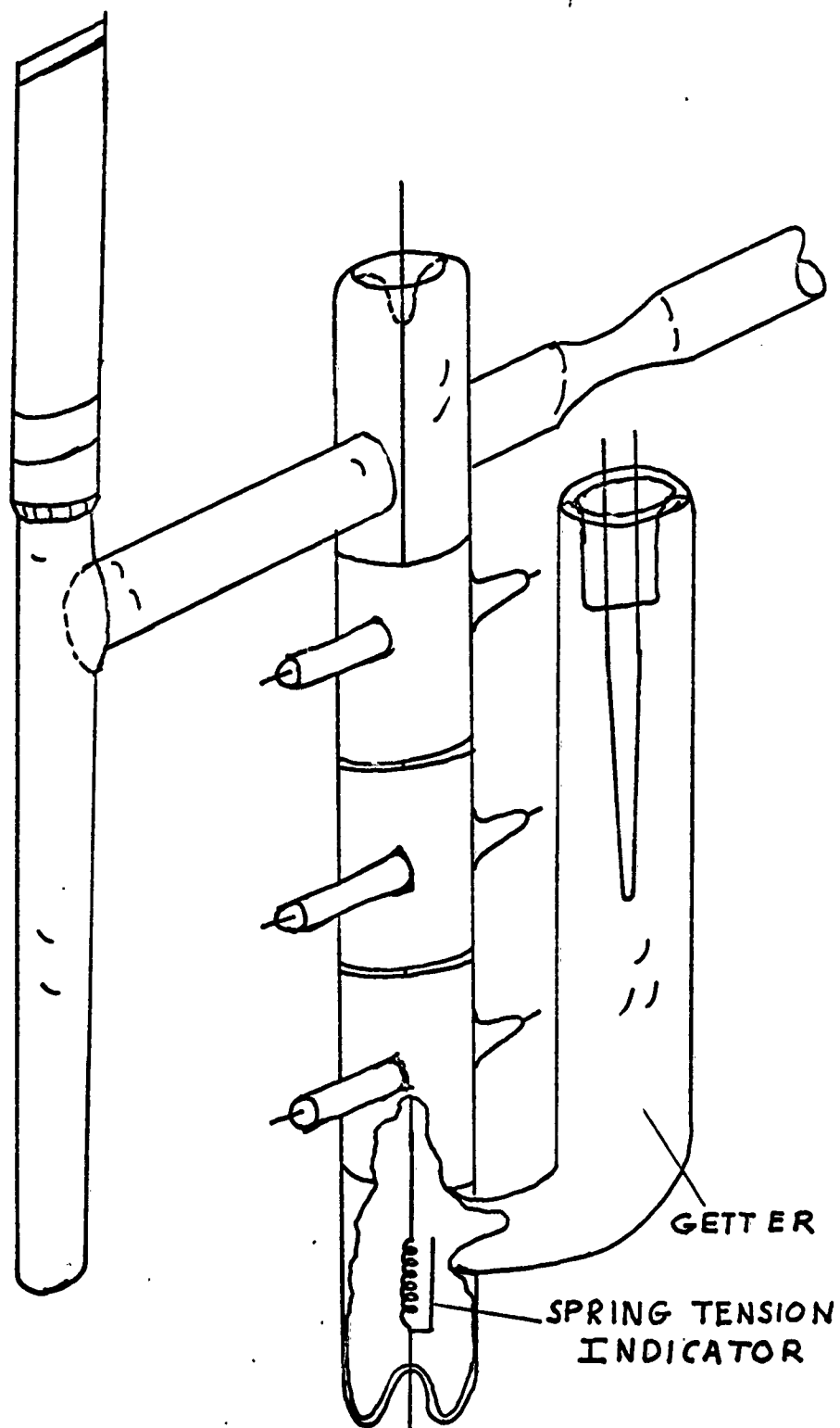


FIGURE 2 SECOND TUBE

REFERENCES

1. Gilleo, M. A., and Kash, S. W., "Propulsion by Composite Beams of Negative and Positive Ions," ARS Report 1157-60.
2. Kilpatrick, W., "Experimental Investigation for Obtaining Stable Negative Ions," NASA Contract No. NAS 5-604, Electro-Optical Systems, Inc. Report 1981, Dec 1961.
3. Trischka, J. W., Marple, D., and White, A., "The Production of Halogen Negative Ions at the Surface of a Thoriated Tungsten Filament," Physical Review, Vol. 85, pg. 136, 1952.
4. Sunderland, R. J., Radbill, J. R., and Gilpin, R. D., "The Development of a Negative Ion Source," ARS Report, No. 1371-60.
5. Taylor, J. B., and Langmuir, I., "The Evaporation of Atoms, Ions and Electrons from Cesium Films on Tungsten," Physical Review, Vol. 44, pg. 423, 1933.
6. Ionov, N. E., "Formation of Negative Ions in the Process of Surface Ionization of Alkali-Halides on Heated Tungsten," Doklady Akademii Nauk S. S. S. R. 28, pg. 512, 1940.
7. Jones, H. A. and Langmuir I., "The Characteristics of Tungsten Filaments as Functions of Temperature," G. E. Review 30, 310, 354, 1927.
8. Langmuir, I., and Blodgett, K. B., "Currents Limited by Space Charge Between Co-Axial Cylinders," Physical Review, Vol. 22, pg. 347, 1923.
9. DelCroix, J. L., "Introduction to the Theory of Ionized Gases," Interscience Publishers Inc., New York, 1960, pg. 33
10. Langmuir, I., and Blodgett, K. B., "The Design of Tungsten Springs to hold Tungsten Filaments Taut," Review of Scientific Instruments, 5, pg. 321, Sep 1934.

11. Honig, R. E., "Vapor Pressures of the Elements," RCA Review 18, pg. 195, June 1957.